

Photodegradation of Pyribenzoxim in Water

Jong-Su Seo · Joon-Kwan Moon · Jeong-Han Kim

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Abstract Photolysis of pyribenzoxim was assessed in various aqueous solutions under sunlight. In direct photolysis, half-lives of pyribenzoxim were 26.9 and 9.2 days for deaerated and non-deaerated distilled water, respectively. Five photoproducts, bispyribac, benzophenone oxime, 2-hydroxy-6-(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid, benzophenone, and 2-hydroxy-6-(4-hydroxy-6-methoxy-pyrimidin-2-yloxy)benzoic acid, were identified after irradiation under a xenon lamp for 4 h. In indirect photolysis, half-lives of pyribenzoxim were 6.0, 3.6, 4.8, 2.2, 11.4, and 9.8 days for humic water, paddy water, rose bengal, Fenton's reagent, furfuryl alcohol, and mixture of furfuryl alcohol and rose bengal. The photolysis rate of pyribenzoxim in Fenton's reagent aqueous solution was faster than other sensitizers. Furfuryl alcohol, a singlet oxygen quencher, inhibited the photodegradation of pyribenzoxim to some extent.

Keywords Fenton's reagent · furfuryl alcohol · photodegradation · pyribenzoxim

Introduction

The use of pesticide is an indispensable part of modern agriculture. Pesticides applied in agricultural fields are subjected to various decomposition pathways. Photolysis is one of the most important pathways of pesticide degradation in water and air, as well as on

plant and soil surfaces (Burkhard and Guth, 1979). Photolysis can be classified as direct and indirect photolysis (Davidson, 1979). Chemicals having strong absorption in the near ultraviolet (UV) or visible (VIS) light range can be decomposed directly by sunlight. Those having negligible light absorption can be broken down by sensitizing mechanisms. For example, chemically active oxygen species produced by various photosensitizers are known to be involved in indirect photolysis (Zhang et al., 2008; Buchalska et al., 2010). Humic substances, riboflavin, and rose bengal are well known examples of direct acting or active oxygen producing sensitizers (Cho et al., 1993; Schwarzenbach et al., 1993; Christopher and Irene, 1996; Gang et al., 1996; Christopher et al., 1999). The Fenton's reagent is a powerful oxidation reagent that attracted interest in waste water treatment, and this reagent involved the hydroxyl radical produced by mixing hydrogen peroxide with ferrous salts (Laurence et al., 1999). Furthermore, furfuryl alcohol is well known as a trapping agent of singlet oxygen (Frank and Jurg, 1987; John et al., 1996; Franklin et al., 1998). Various photolysis were carried out with photosensitizers in aqueous phase (Nowakowska et al., 2001) or soil (William et al., 1980; Partha and Prem, 1997) to evaluate the sensitization characteristics.

Pyribenzoxim [benzophenone *O*-[2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoyl]oxime] is a new postemergence herbicide developed by LG chemical Ltd, Korea, in 1997 and was found to be very effective against barnyardgrass with low application rate (Koo et al., 1997). This herbicide was registered in Asian regions including China, Vietnam, Thailand, as well as Columbia, Nicaragua, Panama in South America. This chemical is relatively immobile and rapidly degraded in soil (Tomlin, 2006). Pyribenzoxim was reported to act rapidly, showing a maximal level of inhibition in whole plants within 24 h after treatment at the target site (Koo et al., 2000). *In vitro* metabolism of pyribenzoxim with rat liver microsome revealed the formation of hydroxylated products, and pyribenzoxim was metabolized into five metabolites via hydrolysis, oxidation, and conjugation with glucuronic acid (Kim et al., 2000; Liu et al., 2005). No significant maternal or embryonic toxicity has been found (Shin et al., 1998), and the bioavailability in rats was negligible, as shown by the elimination of radioactivity

J.-H. Kim (✉)
Department of Agricultural Biotechnology, Seoul National University,
Seoul 151-742, Republic of Korea
E-mail: kjh2404@snu.ac.kr

J.-S. Seo
Environmental Toxicology Research Center, Korea Institute of Toxicology,
Daejeon 305-343, Republic of Korea

J.-K. Moon
School of Plant, Life and Environmental Sciences, Hankyong National
University, Ansung 456-749, Republic of Korea

with feces (88.6%) and urine (8.5%) after 168 h of treatment (Liu et al., 2001). *In vivo* metabolism of pyribenzoxim with rice showed total residue at harvest was less than 0.1% of initial residue, and two major metabolites were identified (Chang et al., 2011).

Little information is available in the open literature on the photodegradation of pyribenzoxim. The present study was conducted to determine the kinetics of sunlight photodegradation in distilled water and the effects of photosensitizers including humic water, rose bengal, Fenton's reagent, and paddy water or furfuryl alcohol as a quencher on the photodegradation rate of pyribenzoxim.

Materials and Methods

Chemicals. Pyribenzoxim, benzophenone oxime, and bispyribac sodium were kindly provided by LG Chemical (Korea). Over 98% pure pyribenzoxim was used without further purification. Benzophenone (99%), humic acid sodium salt (98%), rose bengal (91%), ferrous sulfate (99%), and furfuryl alcohol (99%), were purchased from Aldrich Chemical Co (USA). All high performance liquid chromatography (HPLC) grade solvents and hydrogen peroxide (>28%, H₂O₂) were purchased from Duksan Co. (Korea). Distilled water was filtered through a sybron/Barnstedt Nanopure II water system set at 17.8 MΩ-cm to give deionized-distilled water. Paddy water samples were collected from an experimental farm, Seoul National University, and filtered through a 0.2-μm membrane filter.

Theoretical maximum photolysis rate constant and minimum half-life. Molar extinction coefficient of the test chemical in an aqueous solution (4.6×10⁻⁶ M) was calculated from the UV/VIS spectra of the compound measured with an HP UV/VIS spectrophotometer (Hewlett-Packard, USA). The absorbance was measured between wavelength 297.5 and 800 nm. Maximum photolysis rate constant, (K_{PE})_{max}, and minimum half-life, (t_{1/2})_{min} were estimated with equations 1 and 2, respectively (US EPA, 1998a).

$$(K_{PE})_{max} = \sum \varepsilon_{\lambda} \times L_{\lambda} \quad (1)$$

$$(t_{1/2})_{min} = 0.693 / (K_{PE})_{max} \quad (2)$$

ε_λ = Molar extinction coefficient at wavelength λ

L_λ = Average daily solar irradiance at different seasons and latitudes at wavelength λ

Daily solar irradiance (L_λ) between 297.5 and 1100 nm was measured with a Li-1800 spectrometer (Li-Cor, Inc., USA).

Identification of photodegradation products. Pyribenzoxim (1 mg) dissolved in acetonitrile + water (3+7 by volume; 10 mL) was irradiated under a xenon lamp (1000 W, LH153, Spectral Energy Inc., USA) for 4 h. After irradiation, the sample was partitioned three times with dichloromethane (50 mL). The combined organic fractions were dried over anhydrous sodium

sulfate and concentrated using rotary vacuum evaporator. The residue was redissolved in acetonitrile (5 mL), and an aliquot (20 μL) was analyzed by HPLC. HPLC was performed using an HP 1100 series HPLC system with an HP Zorbax phenyl column (4.6 mm × 250 mm, 5 μm). One-step linear gradient [A = water + 0.1% acetic acid, B = acetonitrile + 0.1% acetic acid: 60% A, 40% B at 0 min; 60% A, 40% B at 3 min; 30% A, 70% B at 7 min] was employed over 30 min at 0.7 mL min⁻¹. UV detection was carried out at 247 nm. For metabolite identification, aliquots were analyzed by liquid chromatography/mass spectrometry (LC/MS) (Quattro LC, Micromass, UK) at electrospray ionization (ESI⁺) mode. The source temperature, desolvation temperature, cone voltage, and capillary voltage were kept at 120, 200°C, 28 V, and 3.29 kV, respectively. Electron multiplier voltage was 640 V. The nebulizer gas and desolvation gas was ultrapure nitrogen set at 80 and 397 L/h, respectively. MS/MS was carried out using nitrogen as collision gas. The collision energy was kept at 65.7 eV. The cone voltage and capillary voltage were adjusted to 25 V and 3.57 kV, respectively.

Photolysis. Sunlight photolysis studies were conducted in Suwon (approximately 36° latitude), Korea, between August 1 and 29, 2000. The aqueous solution of pyribenzoxim (4.6×10⁻⁶ M) was prepared in water + acetonitrile (99+1 by volume) to dissolve the test chemical. The solution (10 mL) was placed in a quartz tube (11 mm i.d., 100 mm length) and irradiated by sunlight. Aliquots (2 mL each) were taken in triplicates after 0, 1, 3, 5, 7, and 14 days of irradiation. The concentration of pyribenzoxim was analyzed in the same manner as mentioned above. Control solutions wrapped with aluminum foil were treated and analyzed in the same manner. To study the effects of aeration on photolysis, each test solution (4.6×10⁻⁶ M) from the above experiments was deaerated with nitrogen gas for 10 min.

To investigate the effects of sensitizers and quencher, an aqueous solution of pyribenzoxim (4.6×10⁻⁶ M) was prepared with rose bengal (17 mM) or synthetic humic acids according to the US EPA method (1998b). Pyribenzoxim was also dissolved in filtered natural paddy water (0.2 μm, Waters, USA), Fenton's reagent, furfuryl alcohol (0.5 mM), and 0.5 mM furfuryl alcohol + 17 mM rose bengal (1+1 by volume) used to determine their photolysis. The Fenton's reagent was prepared by mixing ferrous sulfate (100 μM) with hydrogen peroxide solution (20 mM). Aliquots (10 mL each) of those six solutions were placed in a quartz cell under sunlight as indirect photolysis. The sampling and analysis were carried out with the same method as used in direct photolysis. Dark control solutions in direct and indirect photolysis wrapped with aluminum foil were prepared and analyzed in the same manner.

Because the rate constants from indirect photolysis were the sum of direct and sensitizer-dependent photolysis, sensitized reaction rate was calculated from the following equation (US EPA, 1998b).

$$K_s = K_t - K_d \quad (3)$$

where K_s , K_i , and K_d are sensitized, indirect and direct photolysis rate constants, respectively.

Results and Discussion

Photolysis constants and half-life of pyribenzoxim in distilled water. Average daily solar irradiance and total irradiance during the experimental period were 13.6×10^6 and $340.9 \times 10^6 \text{ J m}^{-2} \text{ day}$, respectively. The molar extinction coefficients of pyribenzoxim was measured for calculation of $(K_{pE})_{\max}$ and $(t_{1/2})_{\min}$. Pyribenzoxim showed maximum absorbance (λ_{\max}) at 194 and 245 nm with negligible absorbance over 330 nm. Because only the light of wavelengths over 290 nm usually arrives onto the earth surface, $(K_{pE})_{\max}$ and $(t_{1/2})_{\min}$ were calculated with wavelengths 297.5–330 nm. The estimated $(K_{pE})_{\max}$ and $(t_{1/2})_{\min}$ were 14.4 day^{-1} and 0.048 days, respectively. The experimental K_{pE} (0.075 day^{-1}) and $t_{1/2}$ (9.2 days) of pyribenzoxim in aerated distilled water showed about 200-fold difference with the corresponding estimated values (Table 1).

Photodegradation products. Irradiation of pyribenzoxim solution under a xenon lamp yielded five photoproducts (Fig. 1). These products were tentatively identified by studying their mass spectra. Tentative assignment of the by-products was made on the basis of molecular ion peaks and fragment ions as obtained from

Table 1 Theoretical and experimental direct rate constants and half-lives in distilled water under sunlight

Parameters		Values
Theoretical values	$(t_{1/2})_{\min}$ (day)	0.048
	$(K_{pE})_{\max}$ (day^{-1})	14.4
Experimental values	$t_{1/2}$ (day) ^a	26.9
	K_{pE} (day^{-1}) ^a	0.026
	$t_{1/2}$ (day) ^b	9.2
	K_{pE} (day^{-1}) ^b	0.075

^ade-aerated, ^bnon-de-aerated

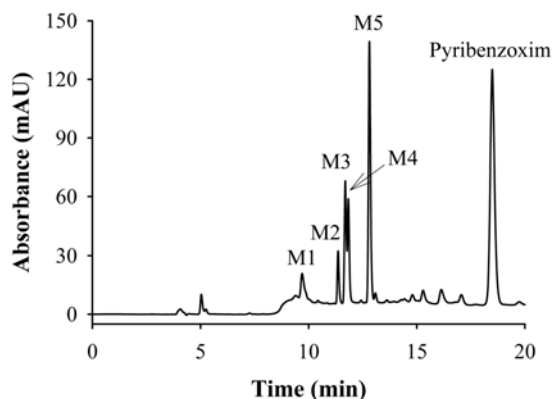


Fig. 1 HPLC elution profiles of a solution of pyribenzoxim irradiated under a xenon lamp for 4 h.

LC/MS and LC/MS/MS experiments, supported by previous knowledge of *in vitro* and *in vivo* metabolism studies of pyribenzoxim (Kim et al., 2000; Koo et al., 2000).

Photoproduct M1 was identified as 2-Hydroxy-6-(4-hydroxy-6-methoxypyrimidin-2-yloxy)benzoic acid (DesMe-HDB) according to its mass spectrum, with a protonated molecule peak at m/z 279 $[\text{MH}]^+$ and characteristic ion fragment peaks at m/z 261 $[\text{MH}^+ - \text{H}_2\text{O}]$ in addition to two other ion peaks at m/z 137 and 125.

Photoproducts M2 was identified as 2-Hydroxy-6-(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (HDB) on the basis of its mass spectrum containing a protonated molecule peak at m/z 293 $[\text{MH}]^+$ and fragment ion peak at 275 $[\text{MH}^+ - \text{H}_2\text{O}]$ in addition to two other ion peaks at m/z 156 and 139. Photoproducts M1 and M2 have been found to result from the metabolism of bispyribac in rats (Fukai et al., 1995).

The mass spectrum of photoproduct M3 showed a protonated molecule peak at 431 $[\text{MH}]^+$ and fragment ion peaks at 413 $[\text{MH}^+ - \text{H}_2\text{O}]$. It was tentatively identified as 2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (bispyribac). A protonated molecule peak at m/z 198 $[\text{MH}]^+$ in the mass spectrum of photoproduct M4 and three other ion peaks at m/z 180, 120, and 77 helped to identify the compound as benzophenone oxime. Photoproduct M5 was tentatively identified as benzophenone, a classic photosensitizer (Morin and Cadet, 1994), according to its mass spectrum, which showed a protonated molecule peak at m/z 183 $[\text{MH}]^+$ and a weak acetonitrile adduct ion peak at m/z 224 $[\text{M} + \text{CH}_3\text{CN} + \text{H}]^+$. Photoproducts M3, M4, and M5 showed identical mass spectra with their authentic compounds. These products are reported in the study of the metabolism of pyribenzoxim in rats and rice (Liu et al., 2005; Chang et al., 2011). After the identification of the various photoproducts, a tentative pathway for the photolytic degradation of pyribenzoxim in water was proposed (Fig. 2). This pathway includes the cleavage of oxime ester bond yielding bispyribac (M3) and benzophenone oxime (M4). Photoproduct M2 (HDB) may be formed from M3 by hydrolysis, and *O*-demethylation of photoproduct M2 yielded M1 (DesMe-HDB). Finally, photo-hydrolysis of M4 gave M5 (benzophenone). Only three photoproducts, bispyribac, HDB, and benzophenone, were detected in paddy water and rose bengal aqueous solution.

Direct photolysis. Sunlight photolysis of pyribenzoxim was performed to study the reaction kinetics. Direct photolysis was carried out as follows: de-aeration by nitrogen gas and nonde-aeration. Direct photolysis rate constants of pyribenzoxim at de-aerated and non-de-aerated samples were 0.026 and 0.075 day^{-1} , respectively (Table 1), indicating that oxygen promoted the photolysis rate by about three times more (Table 1 and Fig. 3). All these values were adjusted by dark reaction.

Indirect photolysis. Photolysis of pesticides in aqueous solutions and on soil and plant surfaces can be altered by various chemicals including humic substances, amino acids, and metals (Kanner and Fennema, 1987; Schwack et al., 1994; Aguer and Richard, 1996; Choudhury and Dureja, 1997; Faure and Boule, 1997; Mazellier et

Fig. 2 Proposed pathway of photodegradation of pyribenzoxim.

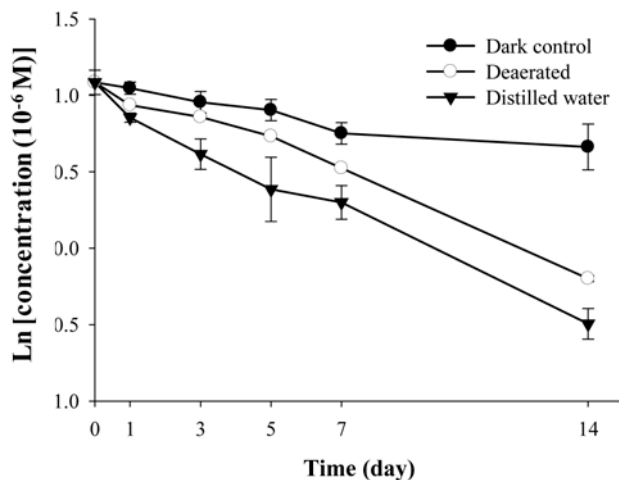
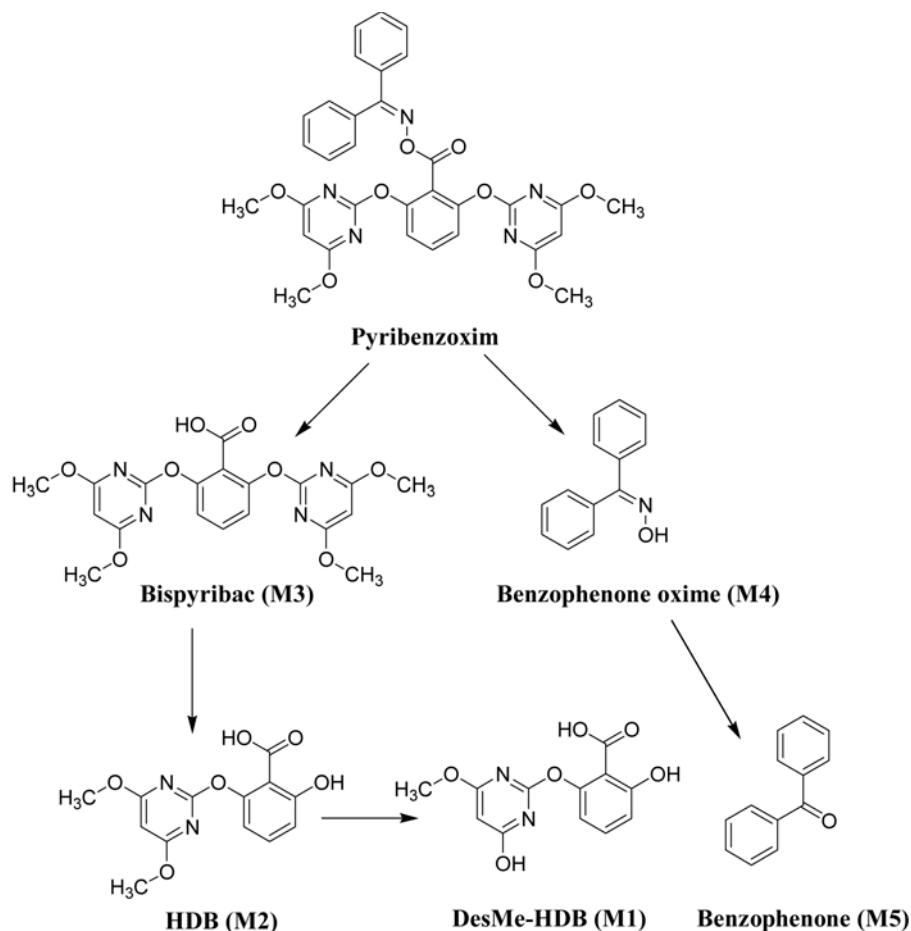


Fig. 3 Direct photolysis kinetics of pyribenzoxim in distilled water.

al., 1997; Misra et al., 1997; Wang et al., 1998). Some chemicals can generate active oxygen species such as singlet oxygen, superoxide radicals, hydroxyl radicals, and hydrogen peroxide that undergo oxidative photodegradation of pesticides.

In the present study, sensitized photodegradation of pyribenzoxim

was measured in aqueous solutions containing humic acid, rose bengal, and Fenton's reagent as well as in filtered natural paddy water. The photolysis rates of pyribenzoxim were slightly increased in humic acid, rose bengal, paddy water, and Fenton's reagent as compared with those in distilled water.

The photodegradation processes followed pseudo-first order kinetics except degradation in solutions containing rose bengal and Fenton's reagent, possibly due to decrease of produced singlet oxygen from these reagents (Table 2 and Fig. 4A). The half-life of pyribenzoxim in Fenton's reagent aqueous solution had about 4-fold difference with the corresponding value in distilled water (Tables 1 and 2). A significant degradation of pyribenzoxim was observed under Fenton's reagent solution, because the ferrous ion (Fe^{2+}) acted as a catalyst producing hydroxy radical (OH^\bullet) from hydroxy peroxide (H_2O_2) (Fig. 4A).

Furfuryl alcohol is well known to be quencher as a trapping agent of singlet oxygen (Frank and Jurg, 1987; John et al., 1996; Franklin et al., 1998). Effects of furfuryl alcohol and rose bengal/furfuryl alcohol mixture on photolysis of pyribenzoxim were studied. Furfuryl alcohol inhibited the photodegradation of pyribenzoxim to some extent (Table 2 and Fig. 4B). The half-life of pyribenzoxim increased slightly in the furfuryl alcohol aqueous solution (Table 2).

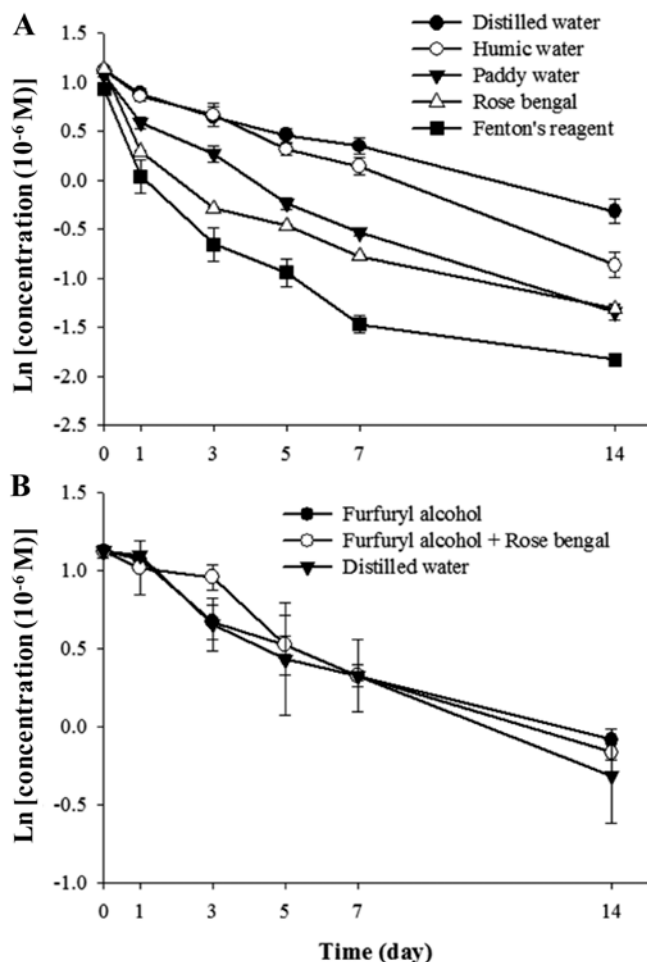
Table 2 Photolysis rate constants and half-lives of pyribenzoxim in various solutions

Media	K (day ⁻¹)	$t_{1/2}$ (day)	R^2
Humic water	0.12	6.0	0.9942
Rose bengal	0.15	4.8	0.8087
Fenton's reagent	0.31	2.2	0.7887
Paddy water	0.19	3.6	0.9513
Furfuryl alcohol	0.061	11.4	0.9439
Furfuryl alcohol + Rose bengal	0.071	9.8	0.9619

Table 3 Comparison between sensitized photolysis and direct photolysis of pyribenzoxim

Media	K_s (day ⁻¹) ^a	K_s/K_d
Humic water	0.040	0.54
Rose bengal	0.070	0.94
Fenton reagent	0.24	3.12
Paddy water	0.17	1.54

^a $K_s = K_t - K_d$, where K_s , K_t and K_d are the sensitized, indirect and direct photolysis rate constants, respectively. The K_d and K_t values are from Table 3.

**Fig. 4** Indirect photolysis kinetics of pyribenzoxim in sensitizers (A) and quencher (B) aqueous solution.

The ratios of sensitized (K_s) and direct (K_d) photolysis constants indicate the effectiveness of sensitizers on photolysis. Sensitized photolysis of pyribenzoxim in humic water, rose bengal, Fenton's reagent, and paddy water aqueous solution was approximately 0.5–3.1 times faster than by direct photolysis (Table 3). The results suggest that photolysis of pyribenzoxim may vary in the environment due to the variability of natural sensitizers, quenchers, and oxygen in natural waters. Chemical sensitization can be the

main driving force of photodegradation of pyribenzoxim in the environment.

In conclusion, the photodegradation of pesticides in water is an area of interesting research and is known to play an important role. We observed that Oxygen in aqueous solution was found to accelerate the photolysis rate of pyribenzoxim in direct photolysis experiment. Effective degradation of pyribenzoxim was feasible by photolysis in the presence of some sensitizers. The photolysis rate of pyribenzoxim in Fenton's reagent aqueous solution was faster than those of other sensitizers due to the sunlight irradiation enhanced the efficiency of the Fenton's reagent (Gustavo and Damia, 1998). Furfuryl alcohol inhibited the photodegradation of pyribenzoxim due to the quenching effect of singlet oxygen.

Pyribenzoxim, in aqueous solution, was photo-degraded via cleavage of oxime ester bond to give bispyribac and benzophenone oxime, which, in turn, were photolyzed into HDB and DesMe-HDB, and benzophenone, respectively. LC/MS was successfully employed for the identification of photoproducts, and MS/MS technique was proved to be an excellent and powerful supplementary tool for confirming the identity of photoproducts.

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